

PREPARATION AND CHARACTERIZATION OF MANGANESE-BASED AND  
CARBON-BASED NANOMATERIALS FOR SUPERCAPACITORS APPLICATION

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## ABSTRACT

In this study, electrochemical materials, namely  $\text{MnO}_2$ , reduced graphene oxide (rGO), porous carbon nanoparticles (PCNs), and rGO/ $\text{MnO}_2$  nanocomposite, were prepared in diverse morphologies such as nanoflowers ( $\text{MnO}_2$ ), nanosheets (rGO), and nanoparticles (carbon). Different physical and chemical characterizations have been conducted to study the structural and morphological properties of the materials under study. Electrochemical properties of the above materials have been studied comprehensively using cyclic voltammetry (CV), galvanostatic charge–discharge (CDC) and electrochemical impedance spectroscopy (EIS) in order to evaluate their suitability as an electrode for supercapacitive energy storage.  $\text{MnO}_2$  nanoflowers were recovered from spent batteries by a combining leaching and electrowinning techniques. The recovered  $\text{MnO}_2$  nanoflowers exhibited high specific capacitance ( $C_s$ ) ( $303 \text{ F g}^{-1}$  at  $5 \text{ mV s}^{-1}$ ). Furthermore,  $\text{MnO}_2$  was electrodeposited by potentiostatic and galvanostatic conditions. Under similar electrodeposition conditions,  $\text{MnO}_2$  deposited by galvanostatic condition showed smaller particle size, less compact layered structure and wider band gap compared to potentiostatic deposition. The galvanostatic  $\text{MnO}_2$  rendered facile ions diffusion, low resistances and showed superior capacitive behavior. The rGO nanosheets were prepared by hydrazine reduction of graphene oxide and their electrochemical properties were studied. The rGO showed high  $C_s$  of 191 and  $168 \text{ F g}^{-1}$  at  $5 \text{ mV s}^{-1}$ , in 5 M KOH and 1 M  $\text{Na}_2\text{SO}_4$ , respectively and high cycling stability  $> 96 \%$  over 1000 cycles. In addition, PCNs with fine particles size of 35 nm were prepared from oil palm leaves using a catalyst free process. The  $C_s$  of PCNs is 245 and  $213 \text{ F g}^{-1}$  at  $5 \text{ mV s}^{-1}$  in 5 M KOH and 1 M  $\text{Na}_2\text{SO}_4$ , respectively. The PCNs showed high cycling stability of 95 %. Practical supercapacitors were developed using rGO and PCNs; the devices delivered energy densities  $\sim 18$  and  $\sim 25 \text{ W h kg}^{-1}$  at power densities 340 and  $360 \text{ W kg}^{-1}$ , respectively, under wider operating voltage window of 2 V in neutral electrolyte. rGO/ $\text{MnO}_2$  nanocomposite has been prepared by simultaneous electrochemical conversion of GO and  $\text{Mn}_3\text{O}_4$ . The  $C_s$  of rGO/ $\text{MnO}_2$  is  $457 \text{ F g}^{-1}$  at  $5 \text{ mV s}^{-1}$ , which are several folds higher compared to those for pure rGO and  $\text{MnO}_2$ . Furthermore, rGO/ $\text{MnO}_2$  showed high stability of 95 % over 2000 CDC cycles. Therefore, the present study identifies electrochemical materials with improved energy storage capabilities.

## ABSTRAK

Dalam kajian ini, bahan electrokimia iaitu  $\text{MnO}_2$ , graphene oksida terturun (rGO), karbon nanopartikel berongga (PCNs), dan rGO/ $\text{MnO}_2$  nanokomposit telah disediakan in pelbagai morfologi, seperti nanobunga ( $\text{MnO}_2$ ), nanolembaran (rGO), dan nanopartikel (karbon). Pelbagai ujian sifat fizikal dan sifat kimia yang berbeza telah dijalankan untuk memahami struktur dan morfologi bahan yang dikaji. Sifat electrokimia telah dikaji secara menyeluruh dengan menggunakan kaedah siklik voltammetrik (CV), galvanostatik cas-discas (CDC) dan electrokimia impedans spektroskopi (EIS) demi menilai kesesuaian sebagai elektrod dalam penyimpanan tenaga superkapasitif.  $\text{MnO}_2$  nanobunga telah didapati kembali daripada bateri terpakai dengan kombinasi kaedah larut lesap dan *electrowinning*.  $\text{MnO}_2$  nanobunga yang didapati kembali menunjukkan kapasitans spesifik ( $C_s$ ) ( $303 \text{ F g}^{-1}$  at  $5 \text{ mV s}^{-1}$ ). Tambahan,  $\text{MnO}_2$  juga dielektrodeposit dengan kaedah potentiostatik dan galvanostatik. Untuk keadaan proses electrodeposit yang sama,  $\text{MnO}_2$  yang dideposit dengan kaedah galvanostatik menunjukkan partikel saiz yang lebih kecil, kepadatan struktur yang rendah dan jurang jalur yang lebih lebar berbanding dengan kaedah potentiostatik.  $\text{MnO}_2$  yang dihasilkan melalui kaedah galvanostatik membenarkan resapan ion yang mudah, rintangan yang rendah dan menunjukkan sifat kapasiti yang lebih baik. rGO nanolembaran telah disediakan melalui penurunan graphene oksida dengan hydrazine dan sifat electrokimia telah dikaji. rGO menunjukkan  $C_s$  yang tinggi iaitu 191 dan  $168 \text{ F g}^{-1}$  pada  $5 \text{ mV s}^{-1}$ , di dalam 5 M KOH dan 1 M  $\text{Na}_2\text{SO}_4$ , masing-masing dan kestabilan kitaran yang tinggi  $> 96 \%$  untuk 1000 kitaran. Tambahan, PCNs dengan partikel saiz yang halus 35 nm turut disediakan dengan daun kelapa sawit tanpa menggunakan pemangkin.  $C_s$  untuk PCNs adalah 245 dan  $213 \text{ F g}^{-1}$  pada  $5 \text{ mV s}^{-1}$  di dalam 5 M KOH dan 1 M  $\text{Na}_2\text{SO}_4$ , masing-masing. PCNs menunjukkan kestabilan kitaran yang tinggi 95%. Superkapasitor praktikal telah disediakan dengan menggunakan rGO dan PCNs dan peranti tersebut menghasilkan tenaga  $\sim 18$  dan  $\sim 25 \text{ W h kg}^{-1}$  pada kuasa 340 and  $360 \text{ W kg}^{-1}$ , masing-masing, di bawah operasi voltan 2 V di dalam neutral elektrolit. rGO/ $\text{MnO}_2$  nanokomposit telah disediakan dengan kaedah pertukaran electrokimia GO dan  $\text{Mn}_3\text{O}_4$ .  $C_s$  untuk rGO/ $\text{MnO}_2$  adalah  $457 \text{ F g}^{-1}$  pada  $5 \text{ mV s}^{-1}$  dan nilai ini adalah beberapa kali ganda lebih tinggi berbanding dengan rGO dan  $\text{MnO}_2$  tulen. Tambahan, rGO/ $\text{MnO}_2$  menunjukkan kestabilan tinggi 95 % untuk 2000 kitaran CDC. Oleh demikian, kajian ini menunjukkan bahan electrokimia yang mempunyai keupayaan simpan tenaga yang ditambahbaikkan.

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## LIST OF SYMBOLS

$\alpha$	Absorption coefficient
$C$	Capacitance
$Q$	Charge
$\Delta t_c$	Charging time
$\eta$	Coulombic efficiency
$B$	Constant relative to the material
$I$	Current
$P_{SXR D}$	Crystalline size
$\theta$	Diffraction angle (degree)
$\Delta t_d$	Discharging time
$S_E$	Electrochemical active specific surface area
$E_g$	Energy band gap
$E$	Energy density
$F$	Farad

$f$	Frequency
$C''$	Imaginary part of the cell capacitance
$Z''$	Imaginary part of the impedance
$m$	Mass of active material
$M$	Molar mass
$n$	Number of electrons
$h\nu$	Photon energy
$\Delta V$	Potential window
$P$	Power density
$C'$	Real part of the cell capacitance
$Z'$	Real part of the impedance
$\tau$	Relaxation time
$\nu$	Scan rate
$k$	Scherrer constant

$C_s$	Specific capacitance
$C_{\text{theo}}$	Theoretical pseudocapacitance
$V$	Volt
$\lambda$	Wavelength



## LIST OF ABBREVIATIONS

2D	Two Dimensional
3D	Three Dimensional
2ES	Two Electrode System
3ES	Three Electrode System
AC	Activated Carbon
ASSCs	Asymmetric Supercapacitors
BET	Brunauer–Emmett–Teller
BJH	Barrett–Joyner–Halenda
CNTs	Carbon Nanotubes
CPE	Constant Phase Elements
CPs	Conducting Polymers
CV	Cyclic Voltammetry
DTA	Differential Thermal Analysis
DFT	Density Functional Theory

ECs	Electrochemical Capacitors
EDL	Electrochemical Double Layer
EDLCs	Electrochemical Double Layer Capacitors
EIS	Electrochemical Impedance Spectroscopy
FESEM	Field Emission Scanning Electron Microscope
FTIR	Fourier Transform Infrared Spectroscopy
GO	Graphene Oxide
HCs	Hybrid Capacitors
JCPDS	Joint Committee on Powder Diffraction Standards
MWCNTs	Multi-Walled Carbon Nanotubes
OCP	Open Circuit Potential
OPL	Oil Palm Leaves
PANI	Polyaniline
PCs	Pseudocapacitors

PCNs	Porous Carbon Nanoparticles
PBS	Phosphate Buffered Solution
PTFE	Polytetrafluoroethylene
rGO	Reduced Graphene Oxide
rGONS	Reduced Graphene Oxide Nanosheets
SSCs	Symmetric Supercapacitors
SWCNTs	Single-Walled Carbon Nanotubes
SWCNHs	Single-Walled Carbon Nanohorns
TEM	Transmission Electron Microscope
TGA	Thermogravimetric Analysis
UV-Vis	Ultraviolet-Visible Spectrophotometry
USEPA	United States Environmental Protection Agency
XRD	X-Ray Diffraction
Zn-C	Zinc-Carbon

## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 CHAPTER OVERVIEW**

This chapter introduces the basic aspects about the materials used in this study and background for the energy storage properties of the materials. Motivation of the research, problem statement, research objectives and scope of work are also presented in this chapter.

#### **1.2 BACKGROUND AND MOTIVATIONS**

Electrochemical capacitors (ECs) are also known as ultracapacitors or supercapacitors. It can be classified into two main categories based on energy storage mechanism, pseudocapacitors (PCs) and electrochemical double-layer capacitors (EDLCs). PCs store electrical energy faradically by electron charge transfer between electrode and electrolyte. Metal oxides and conducting polymers are used as electrode materials for PCs. In EDLCs, a double layer of electrolyte ions is formed on the surface of an electrode material, which arises from the potential-dependence of the surface density of charges stored electrostatically. The electrode materials for EDLCs include all carbon-based materials. Supercapacitors could be used in many applications because of

their higher energy output as compared to conventional capacitors and higher power than batteries, in addition to their miniature size. Various types of electrode materials can be used in supercapacitors, including carbon-based materials, conducting polymers and metal oxides. In addition, the electrolyte could be an aqueous, organic or an ionic liquid. In case of an aqueous electrolyte, the operating voltage is limited to 1 V (due to the electrochemical decomposition of water at 1.23 V), whereas an organic electrolyte can achieve a voltage range of 2.5 to 3.5 V (Syzdek et al., 2014). A higher voltage of up to 4.0 V can be achieved for the ionic liquid. Supercapacitors have many advantages, for example, long life cycles, fast charging time, low impedance and high energy and power density, environmental friendly, and also can be operated in a wide temperature range. This study aims to investigate different materials for supercapacitor applications with high power and long life criteria for better energy storage devices. The energy storage properties are directly depending on the structure and morphology of the electrode materials.

In recent years, manganese dioxide ( $\text{MnO}_2$ ) has drawn increasing attention for supercapacitors application, mainly due to the high abundancy of manganese (Jang et al., 2012) that contributes to low material cost as compared to the expensive ruthenium metal. Pang et al. reported high specific capacitance ( $C_s$ ) ( $700 \text{ F g}^{-1}$ ) for  $\text{MnO}_2$  thin films in year 2000 and their findings had sparked strong interest among energy research community for its application in supercapacitor electrode (Pang and Anderson, 2000, Pang et al., 2000). Such high capacitance value arises from the ions insertion/desertion within  $\text{MnO}_2$  structure and it depends crucially on the particle size, surface area and porosity. Since then, in achieving optimized condition for the aforementioned properties,  $\text{MnO}_2$  with different morphologies have been developed, such as nanoflakes (Chou et al., 2006), nanorods (Yousefi et al., 2012a), nanowires (Yousefi et al., 2013), nanopetals (Yang et al., 2012) and nanosheets (Yan et al., 2012). The synthesis route plays a vital role in determining its morphology. The most common synthesis route for  $\text{MnO}_2$  is chemical coprecipitation method (Deng et al., 2013, Jiang et al., 2009) involving dissolved  $\text{Mn}^{4+}$  precursor. However, instability of  $\text{Mn}^{4+}$  precursor in the aqueous solution as well as the contact resistance between synthesized  $\text{MnO}_2$  and current collectors have hindered its wider use in electrochemical applications (Xu et al., 2008, Prasad and Miura, 2004).

Electrochemical deposition is proven to be an effective method to prepare  $\text{MnO}_2$  nanostructures (Hu et al., 2014, Yousefi et al., 2013).

On the other hand, carbon-based materials possessing high surface area as the electrode material, and the capacitive originates from the charge accumulation at the interface between electrode and electrolyte (Portet et al., 2005). Pseudocapacitors employ transition metal oxides or conductive polymers (Patil et al., 2013, Song et al., 2013, Xie et al., 2012) as the electrode material. Though the energy densities in pseudocapacitors are higher than that of EDLCs, the faradic reactions within pseudocapacitors could lead to phase changes and limit their life time (Compton and Nguyen, 2010). Graphene with its high surface area and nanosheets morphology and carbon nanoparticles with porous structure are a promising materials from energy storage applications.

### **1.3 PROBLEM STATEMENT**

The need for the development of efficient energy storage systems is paramount in meeting the world's future energy targets, especially when the energy costs are on the increase in addition to the escalating demand. Energy storage technologies can improve efficiencies in supply systems by storing the energy when it is in excess, and then release it timely. Nowadays, batteries are slowly becoming obsolete due to their poor cycleability (limited to a few thousands) and long charge time (tens of minutes) in comparison to supercapacitors. On the other hand, supercapacitors have long life time and fast charging times (Vangari et al., 2013). Nowadays the research focus on developed suitable electrode materials which directly reflect in supercapacitor technology enhancement.

$\text{MnO}_2$  has been identified as a promising pseudocapacitive material to replace toxic and costly materials especially ruthenium oxide. Though manganese source can be found abundantly in nature, it is imperative to stop exploiting nature for the advancement of technology. Instead, recovery of manganese from waste sources could be an alternative to obtain  $\text{MnO}_2$ . According to United States Environmental Protection Agency (USEPA) analysis, an average of 8 disposable batteries are consumed by an individual annually.

Annually, around 160 000 tonnes of batteries are placed on the market and around 20 000 tonnes per year of manganese could be recovered (Gallegos et al., 2013). Thus figures raise an alarm on the disposal issue where the common practice in handling spent batteries is landfill which could potentially harm the environment. Furthermore, high percentage of manganese in spent batteries could be a motivation in manganese recovery from batteries to be used as supercapacitor electrode (Sayilgan et al., 2009).

Carbon-based materials are the most widely used materials in commercial supercapacitor. However, activated carbon possesses the problem of achieving high  $C_s$  and thus limiting its wide application in supercapacitor. Graphene possesses high surface area, stable structure and exhibits many interesting electronic, optical and mechanical properties due to its 2D crystal structure. Graphene could be the solution for this problem. On the other hand, as a move to preserve the environment as well as maintain low cost material, waste precursors could be the potential source for the production of carbon-based materials. This include with oil palm biomass residues (leaves, fronds, trunks, empty fruit bunches, shells and fibers) constitute biomass waste produced from oil palm industries which is in abundance in south-east Asia (Chavalparit et al., 2006) (around 73.74 million tonnes per year in Malaysia (Rafatullah et al., 2013)). A common practice in managing oil palm residues is burning which give rise to environmental issues. Furthermore, it is composed of high carbon content (about 18 wt %) (Rafatullah et al., 2013), and could be the potential source for the production of carbon-based material for supercapacitor electrode construction.

EDLCs materials possess good stability but provide with the limited specific capacitance. On the other hand, PCs materials possess good capacitive storage but at a cost of low stability. It is timely to develop a hybrid energy system comprising of both materials and investigating their synergetic effect towards capacitive storage.

## 1.4 OBJECTIVES OF RESEARCH

The objectives of this research are:

1. To determine the physical and chemical characteristics of supercapacitor electrode materials such as  $\text{MnO}_2$ , reduced graphene oxide, carbon nanoparticles and reduced graphene oxide/ $\text{MnO}_2$  nanocomposite.
2. To evaluate the electrochemical characteristics of  $\text{MnO}_2$  recovered from spent batteries as supercapacitor electrode.
3. To evaluate the electrochemical characteristics of reduced graphene oxide from graphite source and porous carbon nanoparticles from biowaste (oil palm leaves) as supercapacitor electrodes.
4. To investigate the synergetic effect of carbon-based nanomaterials and  $\text{MnO}_2$  towards enhanced energy storage properties.

## 1.5 SCOPE OF THE THESIS

The following research activities are required to achieve the mentioned objectives:

1. Recover  $\text{MnO}_2$  from spent batteries through electrochemical method and produce  $\text{MnO}_2$  with different electrochemical approaches.
2. Synthesize reduced graphene oxide nanosheets via modified Hummers' method and produce carbon nanoparticles from oil palm leaves via thermal annealing.
3. Synthesize reduced graphene oxide/ $\text{MnO}_2$  nanocomposite through electrochemical method.
4. Study the structural properties of the synthesized materials with X-ray diffraction, UV spectroscopy, infrared spectroscopy, electron microscopy,  $\text{N}_2$  adsorption-desorption and Raman spectroscopy.
5. Study the electrochemical properties of the synthesized materials with cyclic voltammetry, galvanostatic charge discharge and electrochemical impedance spectroscopy.
6. Fabricate the supercapacitor device with the synthesized materials and evaluate its long term stability.



## **CHAPTER 1**

### **INTRODUCTION**

#### **1.1 CHAPTER OVERVIEW**

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## **CHAPTER 3**

### **EXPERIMENTAL PROCEDURES AND TECHNIQUES**

#### **3.1 CHAPTER OVERVIEW**

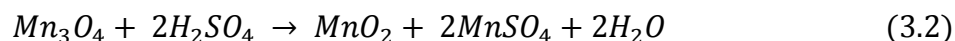
Detailed information about samples preparation for the present research are given in this chapter. The prepared materials for this study are  $\text{MnO}_2$ , reduced graphene oxide, carbon nanoparticles and reduced graphene oxide/ $\text{MnO}_2$  nanocomposite. In addition, this chapter shows a background about chemical and physical characterization techniques, in order to study the properties of the prepared materials such as XRD, FTIR, TGA/DTA, FESEM, TEM, Raman, UV–Vis and  $\text{N}_2$  adsorption–desorption techniques. Finally, the electrodes preparation and cells setup used for supercapacitive testing are mentioned in details.

#### **3.2 SAMPLES PREPARATION PROCEDURES**

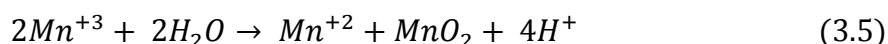
##### **3.2.1 Preparation of $\text{MnO}_2$ from Recycling of Spent Batteries**

A spent Zn–C battery (EVEREADY® D cell) was disassembled and the cathode black paste was taken and used for the subsequent process. The cathode black paste was dried at 130 °C for 24 hours, ground well in a mortar, and then was sieved using 200  $\mu\text{m}$

mesh. The sieved powder was later washed with deionized water (solid to liquid ratio 1:10) in order to remove  $\text{NH}_4\text{Cl}$  electrolyte from the cathode past in the battery and finally dried at  $105\text{ }^\circ\text{C}$  for 24 hours. The dried powder (20 g) was subsequently dissolved in  $\text{H}_2\text{SO}_4$  (200 mL, 2 M, Friendemann Schmidt), followed by addition of  $\text{H}_2\text{C}_2\text{O}_4$  (14.5 g, Aldrich) which act as reducing agent. The leaching process was continued with continuous stirring for 5 hours at  $80\text{ }^\circ\text{C}$  (RÁCZ and Ilea, 2013, Ferella et al., 2008). The reactions which were involved in this preparation are summarized as shown below:



The leached solution was filtered prior to electrowinning. For electrowinning, two stainless steel plates were set up as electrodes and the distance between electrodes was kept at 20 mm. Electrowinning was carried out in 50 mL of leached solution with current density of  $0.15\text{ A cm}^{-2}$  for 1 hour at room temperature. Electrowinning involves Mn(II) oxidation to Mn(III) and followed by disproportionation to Mn(II) and Mn(IV).  $\text{MnO}_2$  was then formed as dark precipitate at the bottom of the cell.  $\text{MnO}_2(\text{Bt})$  was used as a code for the prepared material. The reaction mechanism can be described as follows (Souza and Tenório, 2004):



### 3.2.2 Preparation of MnO<sub>2</sub> by Potentiostatic and Galvanostatic Electrodeposition

MnO<sub>2</sub> was electrodeposited from KMnO<sub>4</sub> solution (0.5 M, Aldrich) by potentiostatic and galvanostatic techniques by applying 10 V and 0.165 A cm<sup>-2</sup> for 30 minutes at room temperature, respectively. Two pre-treated stainless steel plates were used as electrodes. The distance between two electrodes was kept constant at 20 mm throughout the electrodeposition process. For both electrodeposition techniques, black films were obtained on the cathode and the mass was recorded after drying. MnO<sub>2</sub>(PS) and MnO<sub>2</sub>(GS) were used as codes for the prepared materials by potentiostatic and galvanostatic techniques, respectively.

### 3.2.3 Preparation of Reduced Graphene Oxide Nanosheets

Graphene oxide (GO) was prepared from graphite by Hummers' method (Hummers and Offeman, 1958). In order to prevent incomplete oxidation, graphite powder was pre-oxidized by slowly mixed and stirred with graphite (20 g, Merck), K<sub>2</sub>S<sub>2</sub>O<sub>8</sub> (10 g, Aldrich) and P<sub>2</sub>O<sub>5</sub> (10 g, Aldrich) into concentrated H<sub>2</sub>SO<sub>4</sub> (30 mL). The reaction mixture was heated up to 80 °C using an oil bath and continuous stirring for 6 hours. The mixture was then diluted with distilled water, filtered and washed until the filtrate became neutral in pH condition. The washed powder was dried for 8 h in a vacuum oven at 60 °C. The pre-oxidized graphite powder was oxidized as follows: the pre-oxidized graphite powder was added to concentrated H<sub>2</sub>SO<sub>4</sub> (460 mL) cooling in an ice bath. KMnO<sub>4</sub> (60 g) was added to the pre-oxidized solution and continuously stirred over 30 minutes. The mixture was then heated up to 35 °C for 2 hours before distilled water (1 L) was added. The stirring was continued for 15 minutes and additional distilled water (3 L) and 30 % H<sub>2</sub>O<sub>2</sub> (50 mL, Merck) were added onto the mixture. The mixture was then filtered, washed with aqueous HCl (1:10, Merck) and dried in vacuum oven at 60 °C in order to obtain dry graphite oxide. Exfoliation of graphite oxide was done by sonicating graphite oxide dispersion (2 g L<sup>-1</sup>) at 200 W for 30 minutes. The dispersion was later centrifuged at 6000 rpm for 10 minutes to remove the